A STUDY ON THE EFFECTIVENESS OF PLANT EXTRACTS AS CORROSIVE INHIBITORS ON MILD STEEL AND ALUMINIUM

Synopsis

OF THE Ph.D. THESIS TO BE SUBMITTED TO THE

MANGALORE UNIVERSITY

FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

BY

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KARNATAKA, INDIA

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Thesis entitled "A Study on the Effectiveness of Plant extracts as Corrosive Inhibitors on Mild Steel and Aluminium"

Introduction

Corrosion is a phenomenon of destruction and loss of metals and alloys due their chemical or electrochemical reactions on interaction air and moisture. The material destruction poses severe damages in various sectors like construction engineering, defense, machineries, chemical storage units, pipelines etc. Thus the corrosion control has become an issue of prime importance for present day[1]. Among the various corrosion control measures like cathodic protection, anodizing, galvanization, use of corrosion inhibitors had been found to be an important and efficient methods for the prevention of corrosion rate[2]. However, as the synthetic inhibitors are found to be toxic, environmentally hazardous and more costly, the applications of green inhibitors to corrosion medium, prepared from the plant origin, are found to be very economic, eco-friendly and non toxic[3]. Plant inhibitors are found to possess hetero atoms, unsaturated bonds and/or aromatic rings in their structure. These plant chemicals are found to adsorb on the surface of metal alloys and found to block the surface areas by various modes of mechanism, thus retarding the rate of corrosion[4].

In practice, mild steel and aluminium alloys are found to be very useful due to their extensive applications in the field of defense, aerospace industries, medicine, transportation, industries, construction, and in domestic usage[5]. Exposure of these metals to industrial processes likes pickling, etching and to environmental exposure in everyday activities creates their surface loss due to corrosion[6]. Development of a solution for the protection of these metal alloys by corrosion is considered to be a challenging task for today's researchers[7]. Thus in our work we have chosen mild steel and aluminium as target metal alloys and studied the corrosion behavior of those metal under different experimental conditions. The protection efficiency of the plant extracts prepared from different products of *Theobroma Cacao* are studied and the results of the work have been presented in five chapters are as follows.

1. a) Ahmad Zaki, Principles of Corrosion Engineering and Corrosion Control, Elsevier, 2006; b) Fontana Mars Guy, Norbert D. Greene, Corrosion Engineering, McGraw-hill, 2018; c) McCafferty Edward, Introduction to Corrosion Science, Springer Science & Business Media, 2010.
2. a) Bertolini Luca, et al. *J. Appl. Electrochem*, 28(1998): 1321-1331; b) Blawert Carsten, et al. *Adv. Eng. Mater*, 8(2006): 511-533; c) Xu Long, et al. *Prog. Org. Coat.*, 114(2018): 90-101; d) Raja Pandian Bothi, et al. *Chem. Eng. Commun.*, 203(2016): 1145-1156.
3. a) Kesavan Devarayan, et al. *Chem. Sci. Rev. Lett*, 1(2012): 1-8; b) Popoola Lekan Taofeek, *Corros. Rev.*, 37(2019): 71-102; c) Salleh Siti Zuliana, et al. *J. Clean. Prod.* (2021): 127030; d) Chaubey Namrata, et al. *J. Mol. Liq.*,(2020): 114385; e) Buchweishaija Joseph, *Tanz. J. Sci*, 35(2009):77-92.
4. a) Hari Kumar Sappani et al. *Ind. Eng. Chem. Res.*, 52(2013):7457-7469; b) Montemor M. F., *Active Protective Coatings*, Springer, Dordrecht (2016): 107-137; c) Kamal C., M. G. Sethuraman., *Res. Chem. Intermed.*, 39(2013): 3813-3828; d) Sangeetha M., et al. *Port.e Electrochimica Acta*, 31(2013): 44-45; e) Habeeb Hussein Jwad, et al. *Results Phys.*, 8(2018): 1260-1267.
5. a)CabotP.L., et al. *Electrochim. acta*, 36(1991):179-187; b) Oguzie E.E., G.N.Onuoha, E.N.Ejike, *Pigment. Resin Technol.*, (2007):44-49; c) Es'haghi Moosa, et al. *Anti-Corros. Methods Mater.* (2018):310-316; d) Husaini Musa et al. *Bayero J. pure appl. sci. technol.*, 11(2018): 88-92; e) Ameh Paul Ocheje, Nnabuk Okon Eddy, *Res. Chem. Intermed.*, 40(2014): 2641-2649.
6. a) Kamal C., M.G. Sethuraman, *Arab. J. Chem.*, 5(2012):155-161; b) Afia Leila, et al. *Res. Chem. Intermed*, 38(2012): 1707-1717.
7. a) Singh Ambrish, V. K. Singh, M. A. Quraishi. *Int. J. Corros.*, (2010):1-12; b) Verma Dakeshwar Kumar, Fahmida Khan. *Green Chem Lett Rev*, 9 (2016): 52-60.

CHAPTER 1: Introduction and Literature Review

The first chapter of our work includes a detailed description on introduction to corrosion, factors affecting the rate of corrosion, types of corrosion, thermodynamics, impacts of corrosion and the various methods used for the corrosion rate measurements (classical and electrochemical methods). The chapter describes the importance of target metals selection and selection of plant for the study. The chapter includes a brief report on literature study about green inhibition of mild steel and aluminium with discussion on the importance and scope of the present work.

CHAPTER 2: Materials and Methods

The current chapter deals with the materials and methods adopted for the current study. The chapter involves the description on the selection and composition of different target materials, preparation of aggressive medium, selection of the raw materials used for the preparation of green inhibitors. The chapter also includes the explanation on the methods used for the extraction, characterization of plant extracts by spectroscopic approaches (FT-IR and GC-MS), thermal characterization, weight loss measures, EIS study, Tafel study. The description on surface examinations method by SEM is presented in the chapter.

CHAPTER 3: Preparation, Characterization and Thermal decomposition study of *Theobroma Cacao* dry bean, Matured Pod and Tender Pod Extracts

Chapter 3 includes the preparation of green inhibitors from *Theobroma Cacao* plant's beans and pods. The dried beans of cocoa and the pods are collected at matured and tender state and the study was carried out. The study involved the Soxhlet extraction of plant parts with methanol. These extracts were named as Cocoa Dry Bean Extract (CDBE), Matured Cocoa Pod extract (MCPE) and Tender Cocoa Pod Extract (TCPE). The extracts were then characterized using FT-IR and GC-MS. TGA-DTA-DSC study was applied on each extract to check the thermal stability of the extract. FT-IR spectrum of CDBE is shown in Figure 1(a). The spectrum was analyzed and the presence of functional groups such as -CO_2H, -C-O-C, -OH, -NH groups were confirmed. This supported the prediction of adsorption activity of the prepared extracts on the target metal samples[8]. The extracts were also subjected to GC-MS analysis and the different chemical constituents present in the extract were identified. The major chemical constituent identified in MCPE is 1, 2 Bis-(trimethylsilyl) benzene is presented in Figure 1(b).

Thermal stability of the extracts was studied using TGA-DTA-DSC techniques. The phytochemicals identified via GC-MS were correlated to this thermal decomposition through their melting point study. The % weight loss exhibited in TGA-DTA-DSC spectrum was coordinated for the presence of

8. a) Haddadi Seyyed Arash, et al. *J. Mol. Liq.*, 284(2019): 682-699; b) Ram Vijay R., et al. *Int. Lett. Nat. Sci.*, 21(2014):12-20.

cellulose, hemicelluloses derivatives in plant parts[9]. The chapter also includes the details of quantitative estimation of *Kjeldahl Nitrogen* for all three extracts.

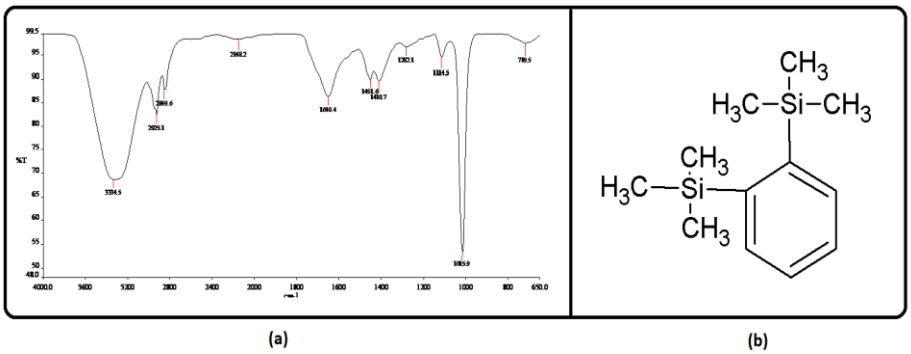

Figure 1: (a) *FT-IR spectrum of CDBE* ***(b)*** *1, 2 Bis-(trimethylsilyl) benzene*

CHAPTER 4: An Investigation of Inhibition Efficiency of CDBE, MCPE and TCPE on Mild Steel in Strong and Weak Acid Medium

The current chapter deals with the experimental details related to investigation of inhibition efficiency of the prepared extracts CDBE, MCPE and TCPE, taking mild steel as target metal. Initially, the mild steel coupons were subjected undergo weight loss study were prepared and inhibition efficiency of the extracts was examined with variation of time at 303 K. The time duration for which the maximum efficiency exhibited by CDBE was found and it is chosen as contact hour of exposure for the specimen sample. The variation of inhibition efficiency for mild steel in 1 M HCl is as shown in Figure 2. Later the variation of inhibition efficiency (% IE) of CDBE was tested with the variation of concentration (% Volume of inhibitor addition) at 303 K for the chosen time interval. The study proved CDBE as a potent inhibitor. There afterwards, in order to compare the behavior of CDBE in weak acid, the similar kind of study is carried out in weak acid medium i.e., 1 M CH_3CO_2H. Similarly, MCPE and TCPE were also tested for their % IE and the corrosion rate variation in 1 M HCl and 1 M CH_3CO_2H and those experimental details are furnished in the current chapter.

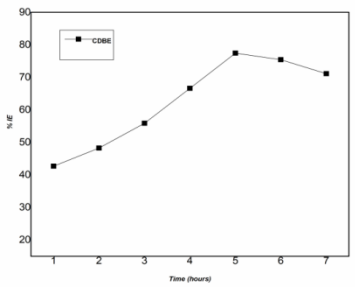

Figure 2: *The variation of inhibition efficiency for mild steel in 1 M HCl with CDBE*

9. a) Hemashree K., J.Ishwara Bhat, *Res. Chem. Intermed.*, 43(2017): 4369-4386; b) P. Chaithra, J. I. Bhat, *Glob. Nest J.* , 19(2017):49-56.

The chapter also includes the study of effect of temperature on variation of corrosion rate for mild steel in both strong and weak acid medium (308 K-323 K) using all three extracts on independent experiments. The details of Enthalpy of reaction (ΔH_a), Entropy of activation (ΔS_a), Arrhenius factor (A) and Energy of activation (ΔE_a) were computed using Arrhenius plots and transition state plots. The study helped us to predict the made of adsorption mechanism and kinetics of inhibition reaction. The sample plots for mild steel with MCPE at a temperature range of 303 K-323 K are as shown in Figure 3.

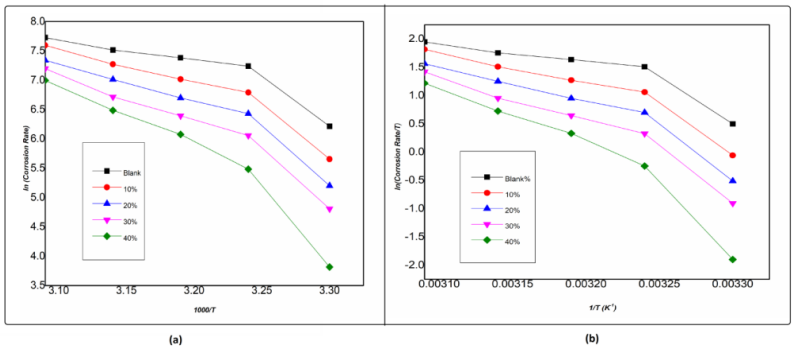

***Figure 3: (a)** Arrhenius plot **(b)** Transition state plot for mild steel in 1 M HCl with MCPE*

Further, the electrochemical methods; *Electrochemical Impedance Spectroscopy* (EIS) and *Potentiodynamic Polarization* techniques furnished the details of corrosion rate and % IE of the extracts, which are presented in this Chapter. Mild steel was subjected to undergo corrosion retardation test at 303 K using CDBE, MCPE and TCPE in 1 M HCl and 1 M CH_3CO_2H medium on separate experiments. The EIS data was interpreted using *ZSimpWin 3.21* for Electrical Equivalent Circuits (EEE) was predicted. The Tafel plot helped us to infer about classification of inhibitor to cathodic, anodic or mixed type. The EIS and Tafel plot for mild steel with TCPE in 1 M CH_3CO_2H at 303 K is shown in Figure 4(a) and Figure 4(b), respectively. The last part of the chapter also contains the details of surface morphological study of mild steel during corrosion; with and without inhibitors at 303 K and the proposed mechanism of corrosion.

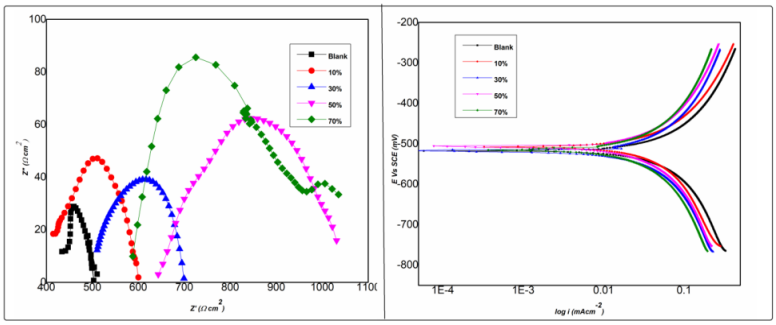

***Figure 4: (a)** EIS plot **(b)** Tafel plot for mild steel in 1 M CH_3CO_2H with TCPE*

CHAPTER 5: Evaluation of CDBE, MCPE and TCPE Performance on Corrosion Mitigation of Aluminium in Acidic and Alkaline Medium

Chapter 5 deals with the results related to the evaluation of % IE of CDBE, MCPE and TCPE on aluminum (*Al-63400*) alloy corrosion in acidic and alkaline medium. 0.5 M HCl and 0.01 M / 0.001 M NaOH were chosen to be aggressive medium for the study. Each inhibitor was tested for its maximum protection efficiency value against corrosion with variation of time by weight loss measurements. The best time duration for which highest efficacy was proved by the green inhibitor was chosen for variation of concentration. The plot of variation of Corrosion rate (CR) with % volumes of MCPE inhibitor is shown in Figure 5. The studies were conducted at different temperature also between 303 K- 323 K and experimental details of the same are provided in current Chapter. In this chapter, the thermodynamics and kinetics of corrosion is also discussed. The study yielded details of enthalpy, entropy, free energy change during the inhibition reaction.

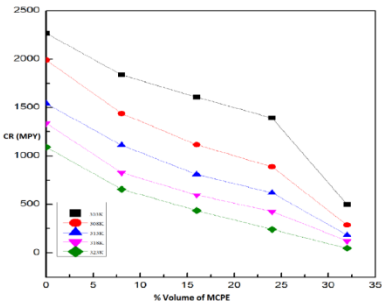

Figure 5: *Variation of CR of MCPE for aluminium with temperature*

The corrosion rate of aluminium, % IE of CDBE, MCPE and TCPE for aluminum in HCl and NaOH medium are presented in the Chapter 5. The Chapter also covers the details about the studies of aluminium corrosion rate and % IE of the extracts prepared, as checked by EIS and Tafel method at 303 K in acidic and alkaline medium. The plots of EIS and Tafel for aluminum in basic medium for TCPE inhibitor is shown in Figure 6(a) and Figure 6 (b), respectively.

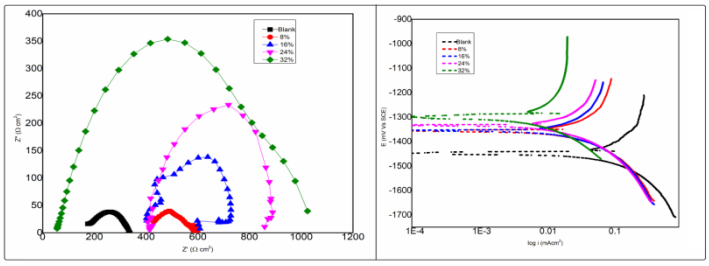

Figure 6: (a) *EIS* ***(b)*** *Tafel plots for aluminum with TCPE in NaOH*

The surface microstructure of aluminum is studied in acidic and basic medium using CDBE, MCPE and TCPE in separate experiments. The surface porosity reduction was clearly observed supporting the inhibitor action by adsorption mechanism. The figures showing the surface destruction of aluminum in 0.5 M HCl and protection by CDBE are shown in Figure 7(a) and Figure 7 (b), respectively. The mechanism of corrosion inhibition in acidic and basic medium is also discussed in the current chapter with comparison of results and conclusions.

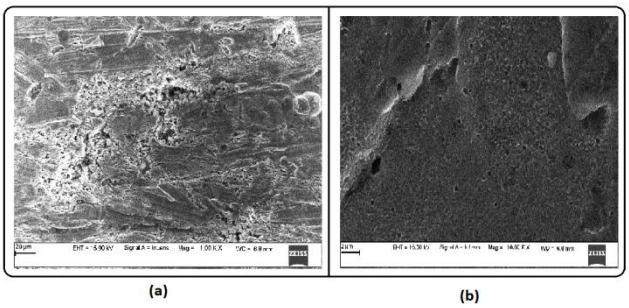

***Figure 7: (a)** SEM images of aluminum in HCl **(b)** aluminum in HCl with CDBE*

Summary and Scope of Work

As the conclusive part of the thesis, the summary narrates the comparative account of inhibitory actions exhibited by CDBE, MCPE and TCPE in different aggressive medium for the chosen target alloys. The content also explains the salient features of the work and scope of current research for the society with its significance.

List of publications

A. Papers Published in International Journals

1. P. Shwethambika, J. Ishwara Bhat, "*Theobroma Cocoa* Dry Bean Extract as a Potential Green Inhibitor for Mild Steel in Acidic Medium" *Iranian (Iranica) Journal of Energy and Environment*, 10(3):190-199, 2019.
2. P. Shwethambika, Ishwara J. Bhat, "Matured *Theobroma Cocoa* Pod Extract as green inhibitor for acid corrosion of aluminium", *Iranian Journal of Chemistry and Chemical Engineering(IJCCE),* 4(3):906-919,2021.
3. Pernaje Shwethambika, Ishwara J. Bhat, Mahagundappa R. Maddani, "A chemical and electrochemical investigation on mitigation of acidic and alkaline corrosion for *Al-63400* alloy using tender cocoa pod extract", *Journal of Bio-and Tribo-Corrosion,* 7(3):1-13,2021.
4. Pernaje Shwethambika, Ishwara J. Bhat, Mahagundappa R. Maddani, "Spectroscopic characterization and evaluation of tender *Theobroma cacao* pod extract as eco friendly inhibitor for mild steel in 1 M HCl", *Research on Chemical Intermediates,* 47:5369–5388, 2021.

Research articles under construction

1. Pernaje Shwethambika, Ishwara J. Bhat, Mahagundappa R. Maddani, "A comparative study of Cocao dry bean extract as potent green inhibitor for aluminium under strong and weak acid medium"

2. Pernaje Shwethambika, Ishwara J. Bhat, Mahagundappa R. Maddani, "An investigative study on corrosion protection efficacy of *T.Cacao* bean and pod extracts on Mild steel in 1 M CH_3CO_2H"

B. Papers presented in National/International Conference

i. Presented a research paper entitled **"***Spectroscopic and thermal characterization of theobroma cocoa bean extract and its study of anti-corrosive property"* in an international conference 'RAMSB-2018' held at Mangalore University, Mangalagangothri (January 23-25, 2018).

ii. Presented a research paper entitled *"Matured cocoa pod extract as a green inhibitor towards the corrosion inhibition of aluminium in acidic medium"* in 37th national conference of Indian Council of Chemists held at NITK, Surathkal (December 12-14, 2018).

iii. Presented a research paper entitled "*A study of cocoa dry bean extract (CDBE) as a potential inhibitor for the corrosion of aluminium in acid medium"* in national conference 'RIMMC-2019' held at Mysore University, Manasagangothri (March 8-9, 2019).

iv. Presented a research paper entitled "*Spectroscopic characterization of matured theobroma cocoa pod extract and study of its anticorrosive property"* in an international conference 'AFMHCC-2019' held at Mysore University, Manasagangothri (March 18-20, 2019).

v. Presented a research paper entitled "*Spectroscopic characterization of tender cocoa pod extract and study of its anti-corrosive property*" in a national conference 'NCASEM-2019' held at Vivekananda college of Engineering and Technology, Puttur (August 23-24, 2019).

vi. Presented a research paper entitled "*Spectroscopic characterization of matured theobroma cocoa pod extract and study of its anticorrosive property"* in an international conference 'ICCM-2019' held at Mangalore University, Mangalagangothri (October 17-19, 2019)

Ms. Shwethambika P. (Research Scholar)

Dr. Mahagundappa R. Maddani (Research Supervisor)